STEMFLOW ACID NEUTRALIZATION CAPACITY

IN A BROADLEAVED DECIDUOUS FOREST:

THE ROLE OF EDGE EFFECTS

by

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Honors Bachelor of Science in Chemistry and Environmental Science with Distinction

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ABSTRACT

Atmospheric deposition is an important pathway for moisture, nutrient, and pollutant exchange among the atmosphere, forest, and soils. Previous work has shown the importance of proximity to the forest edge to chemical fluxes in throughfall, but far less research has considered stemflow. This study examined the difference in acid neutralization capacity (ANC) of stemflow of nineteen *Liriodendron tulipifera* L. (yellow poplar) trees between the forest edge and interior in a rural area of northeastern Maryland. We measured ANC directly via potentiometric titration. Stemflow from trees at the forest edge was found to have significantly higher and more variable pH and ANC than in the forest interior ($p < 0.01$). No mathematical trend between ANC and distance to the forest edge was observed, indicating the importance of individual tree characteristics in stemflow production and chemistry. These results reaffirm the importance of stemflow for acid neutralization by deciduous tree species.

Chapter 1

INTRODUCTION

Atmospheric aerosols interact with the environment in many ways. In temperate forests, the dominant mechanisms are wet deposition—particles dissolved in rain and snow—, dry deposition—airborne solids and gases—, and occult deposition—particles dissolved in "cloud" droplets (e.g., mist, fog) (Weathers and Ponette-González, 2011). The rate and characteristics of atmospheric deposition are affected by a number of factors, including proximity to emission sources (e.g., Likens et al., 2005; Weathers et al., 2006; Ponette-González et al., 2010; Weathers and Ponette-González, 2011), climate (e.g., Burkhardt and Eiden, 1994; Bruijnzeel and Proctor, 1995; Behera et al., 2013), and vegetation type (e.g., De Schrijver et al., 2004; de Vries et al., 2007; Ponette-González et al., 2010). In a study of throughfall fluxes in forests and coffee plantations, Ponette-González et al. (2010) observed nitrogen and sulfur concentrations eight and nine times greater in locations influenced by anthropogenic emissions compared to remote sites. In a review of the atmospheric chemistry of ammonia, Behera et al. (2013) argued that relative humidity, temperature, time of day, and atmospheric conditions are all major factors influencing dry deposition velocity. de Vries et al. (2007) found substantial variation in nitrogen deposition fluxes among tree species, with lower fluxes in pine and spruce as compared to deciduous tree species. Oppositely, De Schrijver et al. (2008) witnessed higher throughfall deposition of sulfur and nitrogen in coniferous than in deciduous forests.

Atmospheric deposition is an important pathway for moisture, nutrient, and pollutant exchange between the atmosphere and soils, evidenced by the spatial heterogeneity in forest soil solution chemistry as a function of distance from tree boles (Chang and Matzner, 2000; Jung and Chang, 2013). For instance, throughfall and stemflow deliver toxic trace metals (Avila and Rodrigo, 2004) and nitrogen and sulfur (Vanguelova et al., 2010) to soil in elevated concentrations compared to bulk precipitation. Deposition of acid (H^+) and acid anions (such as NO_3^- and SO_4^{2-}) promotes soil acidity and stimulates leaching and consequent loss of base cations (such as Mg^{2+}, K^+, and Ca^{2+}), many of which are essential plant nutrients (Lovett et al., 1985; De Schrijver et al., 2004; Likens, 2013). This process has been reported to promote soil acid infertility, characterized by elevated Al or H^+ toxicity and nutrient deficiency, as well as accelerated soil podzolization (Wolt, 1990; Neary and Gizyn, 1994). However, atmospheric deposition can also alleviate acid inputs to the soil. Neary and Gizyn (1994) found that throughfall and stemflow enriched in base cations by canopy leaching neutralized acidic inputs in a deciduous forest plot, and suggested that this process is important to forests containing sandy, acidic soils with low cation exchange capacity and base saturation. Amezaga et al. (1997) found that enhanced leaching and canopy washoff of base cations , especially in deciduous trees, successfully buffered the acidification expected as a result of regional sulfate and inorganic nitrogen pollution. Several other studies have reported higher acid buffering capabilities for broadleaved as compared to coniferous tree species. For instance, Jung and Chang (2013) observed increasingly acidic soils around the tree boles of jack pine—attributed to greater deposition of sulfate and nitrate—but increasingly alkaline soils around the boles of aspen—attributed to greater leaching of base cations.

Similarly, using a pH-imaging microscope, Kikuchi (2006) found that deciduous leaves diluted and neutralized artificial acid droplets more effectively than coniferous leaves, although the absence of a spatial effect suggested that this capability was inherent to the leaves rather than a result of deposition or other external forces.

Although the concentrations of individual ions and elements is useful for in-depth mechanistic analysis, the net balance of acid anions and base cations—acid neutralization capacity (ANC)—studies—including those mentioned above—addressed this question through basic charge balance calculations, but alternative indicators have also been used. One metric is the molar ratio of Ca and Al concentrations has been used as an effective gauge of soil stress (Cronan and Grigal, 1995), although the universal applicability of this metric has been contested (Lange et al., 2006). Alternatively, Larssen and Carmichael (2000) used the ratio of sulfur and calcium—the dominant anion and cation—as an indicator of acid excess. Titration is the only method that definitely detects all basic components, although it does not provide any information about the elemental/ionic composition of samples (van Loon and Duffy, 2011). Only one study known to the authors has attempted to measure stemflow ANC via titration: Wang et al (2004), working in Taiwan, reported ANC values that were highly negative for stemflow in a China-fir plantation, but positive for stemflow in secondary and natural hardwood stands. Unfortunately, this study was limited to two rainfall events.

Depositional fluxes are not spatially homogeneous; rather, they have been found to vary substantially as a function of tree position relative to the forest edge. Neal et al. (1994) observed that trees at the forest edge are particularly efficient at scavenging aerosols, evidenced by increased concentrations of many solutes in their

throughfall and stemflow as compared to trees in the forest interior. Devlaeminck et al. (2005) observed an exponential decay in deposition of base cations with increasing distance to the forest edge. Based on a review of literature on edge effects, De Schrijver et al. (2007) found median edge multipliers of 1.21, 1.60, and 1.50 for sulfate, nitrate, and ammonia, respectively. Edge effects are not homogeneous across forest types. As an explanation for the greater edge effects in pine stands compared to deciduous stands, Draaijers (1993) suggested that the magnitude of edge effects increases with higher stand density and lower canopy openness. This suggestion was confirmed by Wuyts et al. (2008), who observed significantly higher edge effects in pine stands than oak stands—attributable to greater stand density and lower canopy openness—but no difference between oak and birch stands—due to the conflicting influences of these two factors. The shape of forest edges also plays a role, with gradual edges receiving less enhanced deposition than sharp edges (Wuyts et al., 2009). Although multiple studies have investigated the role of edge effects in throughfall, stemflow remains a relatively understudied phenomenon.

This study investigates the role of edge effects in the spatial variability of stemflow pH and ANC for *Liriodendron tulipifera* L. (yellow poplar). In particular, the objectives of this study are threefold: (1) to compare the pH and ANC of stemflow from trees at the forest edge to those in the interior of the forest; (2) to investigate the sign and strength of correlations between meteorological conditions (e.g., wind speed and direction, rainfall intensity) and stemflow ANC and pH; and (3) to examine the relationship between tree height- trunk circumference product on stemflow ANC and pH. Such work would increase our knowledge of forest biogeochemical cycling, and specifically forests' vulnerability to soil acidification.

Chapter 2

MATERIAL AND METHODS

2.1 Study area

Field observations were conducted at an experimental watershed within the Fair Hill Natural Resources Management Area in northeastern Maryland (39º42' N, 75º50'W). The study area was selected for the following reasons: (1) accessibility; (2) availability of a wide range of auxiliary ecosystem, soil, and meteorological data; (3) representativeness of mid-Atlantic deciduous forests.

The climate at Fair Hill is primarily humid maritime with well-defined seasons due to proximity to the Delaware and Chesapeake Bays. Convective precipitation patterns dominate summer, while the remaining seasons experience primarily frontal precipitation patterns. Mean 30-year (1981-2010) total annual precipitation is approximately 1200 mm. Summer is the wettest season (314 mm) and winter is the driest season (280 mm). The highest and lowest mean monthly air temperatures are 25.7 ℃ in July and −0.1℃ in January (MD State Climatologist Office, 2014). Hourly meteorological data, including precipitation, air temperature, relative humidity, atmospheric pressure, wind speed and direction, and volumetric soil water content was obtained from a nearby Delaware Environmental Observing System (DEOS) site.

The forest canopy within the study area is deciduous with the dominant species being Fagus grandifolia Ehrh. (American beech), Liriodendron tulipifera L. (yellow poplar), Acer rubrum L. (red maple), and Quercus spp. (oak). The site stand density is 225 trees ha^{-1}, stand basal area is 36.8 m^2 ha^{-1}, mean DBH is 40.8 cm, and mean tree

height is 27.8 m. Stand basal area is 40% poplar, 35% beech, 5% maple, 14% oak, and 6% others. The stand leaf area index (LAI) for edge and interior locations was 3.79 ± 0.41, as measured in early October. As expected, these values are lower than those based only on interior readings at the same study site (e.g., Levia et al., 2011b) due to both a thinner canopy at the forest edge as compared to the interior and the earlier start of leaf abscission and drop from an unusually dry late summer and early fall.

2.2   Field procedure

Nineteen L. tulipifera trees were selected for study from representative locations within the experimental watershed (Figure 1). Individual trees were classified by letter as edge ("E") or interior ("A", "B", "C", with approximate increasing distance from the forest edge), and numbered arbitrarily within each class. Only one tree species was studied to allow us to examine edge effects without the confounding effects of species. Liriodendron tulipifera was selected because it was one of the most prevalent species on-site, and because the combination of lower stemflow volumes (compared to, for instance, F. grandifolia; Levia et al., 2010) and enhanced scavenging of atmospheric aerosols by its rough bark (Levia et al., 2011b) result in easily collectible and highly concentrated stemflow. The diameter at breast height (dbh, 1.37 m) of selected trees ranged between 24.0 to 91.5 cm with a mean value of 54.4 cm. The six trees considered to be on the forest edge had a mean distance of 11 m and a range of 8 to 15 m from the trunk to the outermost reach of the canopy (Figure 1). For the remaining trees, the mean distance was 58 m, with a range of 19 to 126 m. The transect cardinal orientation had a range of 53º to 130º and a mean value of 86º (Table 1). Tree height was measured using a Laser Technology TruPulse 360° laser rangefinder based on measurements of horizontal distance and descending

and ascending angles. The mean height for edge trees was 18.9 m with a range of 15.4 to 26.5 m, while the mean height for interior trees was 24.2 m with a range of 16.1 to 31.4 m (Table 1).
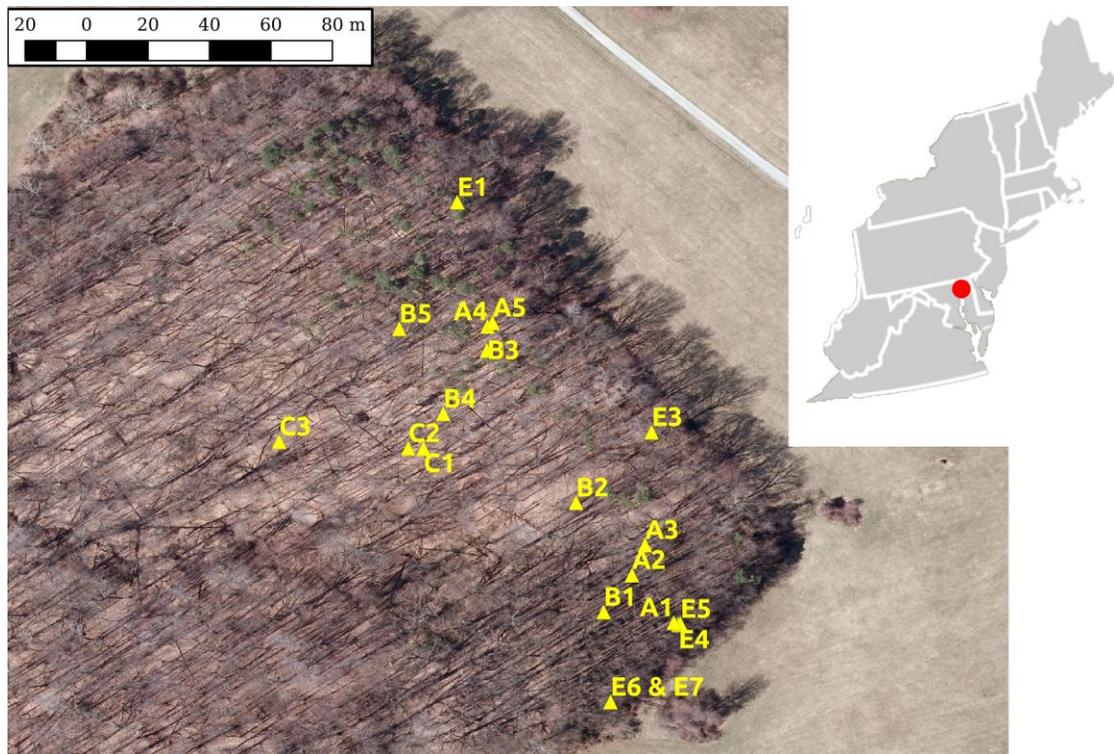
Figure 1. Aerial photograph of study site with sampling tree locations. The tree pairs "E4" and "E5" as well as "E6" and "E7" are marked as a single point because their proximity to each other (< 2 m) prevented them from being distinguished via GPS.

A total of 12 rainfall events were sampled between July 2013 and February 2014, with the majority of events collected during the wet summer months. Stemflow from each selected tree was collected in chemically inert HDPE bins via collars fabricated from longitudinally cut 31.8 mm vinyl tubing and fastened to the tree trunk

with silicone sealant. To prevent inter-event contamination of samples, bins were also lined with polyethylene liners that were replaced after each collection. The maximum stemflow volume that could be accommodated using this method was ~110 L. Stemflow volume was measured and samples collected for chemical analysis as early as possible after each event (usually within 1-2 days). Volume was measured as water depth inside the bins and converted to volume by multiplying by an empirically determined factor of 0.1641 L cm^{-1}. Unfiltered samples were refrigerated (~4ºC) prior to chemical analysis.

Table 1. Summary statistics of canopy structural characteristics of sampled edge and interior trees.

	n	DBH (cm)	Trunk basal area, (cm^2)	Distance to edge (m)	Edge orientation (°)	Tree height (m)	Height-trunk circumference product (m^2)
Edge	6	54.4 (23.5)	2686.8 (2145.4)	11.0 (2.7)	102.8 (34.6)	18.9 (4.8)	34.6 (21.8)
Interior	12	51.1 (21.5)	2387.1 (1836.1)	57.6 (28.6)	78.2 (27.1)	24.2 (5.8)	41.3 (22.6)
All	19	52.2 (21.6)	2481.8 (1883.2)	42.9 (32.3)	85.9 (31.0)	22.6 (5.9)	39.2 (21.9)

* Mean values (± 1 SD)

2.3   Chemical analyses

The pH of each sample was measured in the lab with a Fischer Scientific Accumet Basic pH meter at room temperature (~19-21ºC). ANC was measured by potentiometric titration with a strong acid titrant, following the standard protocol of the United States Geological Survey (Rounds, 2006). Titrant solutions were prepared from concentrated trace-metal grade hydrochloric acid diluted in nanopure water to

concentrations around 20 mM (actual concentrations varied, but were known precisely). A buret micrometer was used to incrementally add precise volumes ($\pm$ 0.005 mL) of titrant to the sample while the resulting pH chance was continuously monitored. The equivalence volume (V_e) was defined as the volume triggering the greatest change in pH, determined via a plot of change in pH vs. change in volume. The ANC of the sample was calculated as

$$\text{ANC, } \mu\text{M} = [\text{HCl, M}] \times \left(\frac{V_e, \text{mL}}{100 \text{ mL}} \right) \times 10^6$$

2.4 Data analysis

Descriptive statistics comparing pH, ANC, and volume across individual trees and for all edge and interior trees were calculated. Non-parametric tests of significance were used due to the heavy positive skewness of the data and limited number of events sampled, recognizing that such tests are less efficient and ignore more sample information than their parametric counterparts (Hoshmand, 1998). The Mann-Whitney U Test was used to test differences in median pH and ANC between edge and interior trees. This test assumes a random sample, a measurement scale that is at least ordinal, and independence within and between samples (Hoshmand, 1998). The $\chi 2$ tests of independence and goodness-of-fit were used to investigate bias in the model of ANC as a function of pH. The only requirements of these tests are independence between and within samples and that events not be exceedingly rare (Hoshmand, 1998). Correlations between variables related to stemflow, tree structure, and meteorological conditions were investigated using Pearson product-moment correlation, which sacrifices statistical robustness and efficiency (especially for non-normally distributed

data) in exchange for broad applicability and ease of interpretation (Sokal and Rohlf, 1995).

André et al. (2008) found that the product of tree trunk circumference and height successfully explained much of the inter-individual variability of stemflow chemistry. This metric was also calculated in this study as a component of the investigation of tree structure influences on stemflow volume, pH, and ANC. Another useful metric used in many stemflow studies (e.g., Park and Hattori, 2002; Murakami, 2009; Levia et al. 2010; Levia et al. 2011a) is the funneling ratio, defined by Herwitz (1986) as

$$F = \frac{S}{P \times B}$$

where S is stemflow volume, P is rainfall depth equivalent, and B is trunk basal area.

The overwhelming majority (95%) of ANC measurements fell in the range of 0 to 2000 μM. The remaining 5% of values were between 2000 and 15,000 μM, which were deemed unrealistically high and therefore excluded from subsequent data analysis. An analysis of the probability density plot for the entire data set showed that the values removed were isolated cases that did not significantly impact the data distribution. The cause of such high values was most likely contamination of samples with non-foliar organic matter (e.g., insect carcasses).

Also, several of the rain events sampled in this study caused certain trees to generate more stemflow than could be collected in a single collection bin. As such, reliable volume estimates for these trees during such events could not be obtained and were excluded from analyses of stemflow volume.

Chapter 3

RESULTS AND DISCUSSION

3.1 Acid neutralization capacity

Taken together, edge trees had a median stemflow ANC of 278.25 μm while interior trees had a median of 113.75 μm, and this difference was statistically significant ($p < 0.01$) (Figure 2). This interior-edge multiplier of 2.44 is considerably greater than those reported by De Schrijver et al. (2007), although this may be because the latter values were only for acid anions and ammonia and did not consider cationic dust. Alternatively, this may be explained by the fact that stemflow is more concentrated than throughfall in most solutes (Levia et al., 2011a). Median stemflow ANC for interior trees was approximately one order of magnitude greater than ANC values reported by Wang et al. (2004) for secondary and natural hardwood stands. However, values for interior trees appear reasonable given the relative concentrations of base cations and acid anions in stemflow reported by Foster and Nicolson (1988), Neary and Gizyn (1994), and Levia et al. (2011b). The variability of stemflow ANC was also greater for edge trees than interior trees, with interquartile deviation values of 134.75 μm and 54.74 μm, respectively (Figure 2). This finding is notably distinct from Devlaeminck et al. (2005), who observed no trend between distance from forest edge and coefficients of variation for throughfall chemical composition.
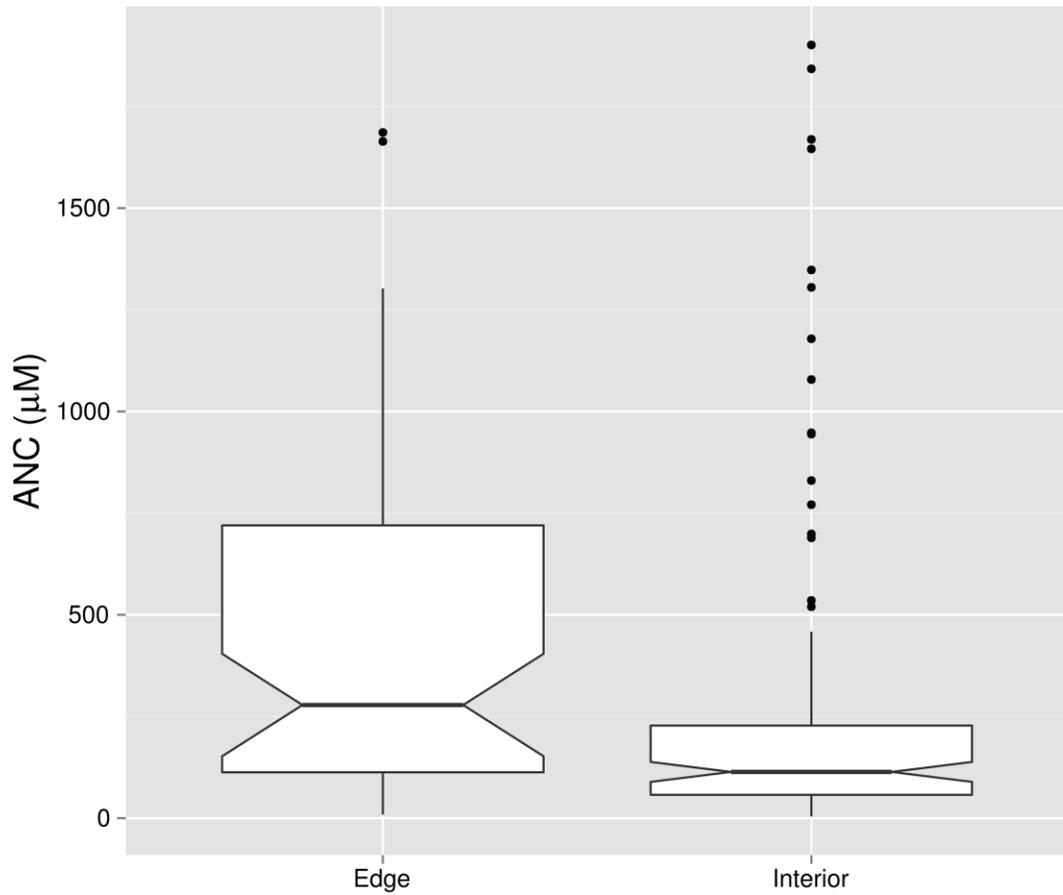
Figure 2. Comparison of stemflow acid neutralization capacity of L. tulipifera trees located at the forest edge and in the forest interior. Boxes are bounded by the lower and upper quartiles, with the median represented by a solid black line. The ends of notches are calculated as $X + 1.58 \text{ IQR} \div n^{1/2}$ (where X is the median, IQR is the interquartile range, and n is the sample size), with non-overlapping notches a likely indication of statistical significance (Chambers et al. 1983). Box tails extend to lowest or highest data value within 1.5 IQR of the lower and upper quartile, respectively. All values outside this range are represented as outliers with dots. $n = 58$ for edge trees and $n = 120$ for interior trees.

On a tree-by-tree basis, these trends are less obvious. The stemflow ANC of all trees was positively skewed, but edge trees generally exhibited greater deviation from the median (Figure 3). However, two trees in particular—"E1" and "C1"—had considerably higher median stemflow ANC than the remaining trees (Figure 3). Tree "C1" also had an uncharacteristically high variability in stemflow ANC, higher than any other interior tree and even most edge trees (Figure 3). No clear trend for stemflow ANC as a function of tree distance from the forest edge (for instance, the exponential decay for throughfall reported by Devlaeminck et al. (2005)) was observed for interior trees (Figure 3). This may be partly attributed to the fact that stemflow is much more variable in terms of volume and chemistry than throughfall (Puckett, 1991; Levia et al., 2011a). Stemflow production, for instance, is more influenced by canopy structure (Levia et al., 2014) than throughfall, which is most generally linearly related with rainfall magnitude (e.g., Crockford and Richardson, 2000; Levia and Frost, 2006; Zimmermann et al., 2008).
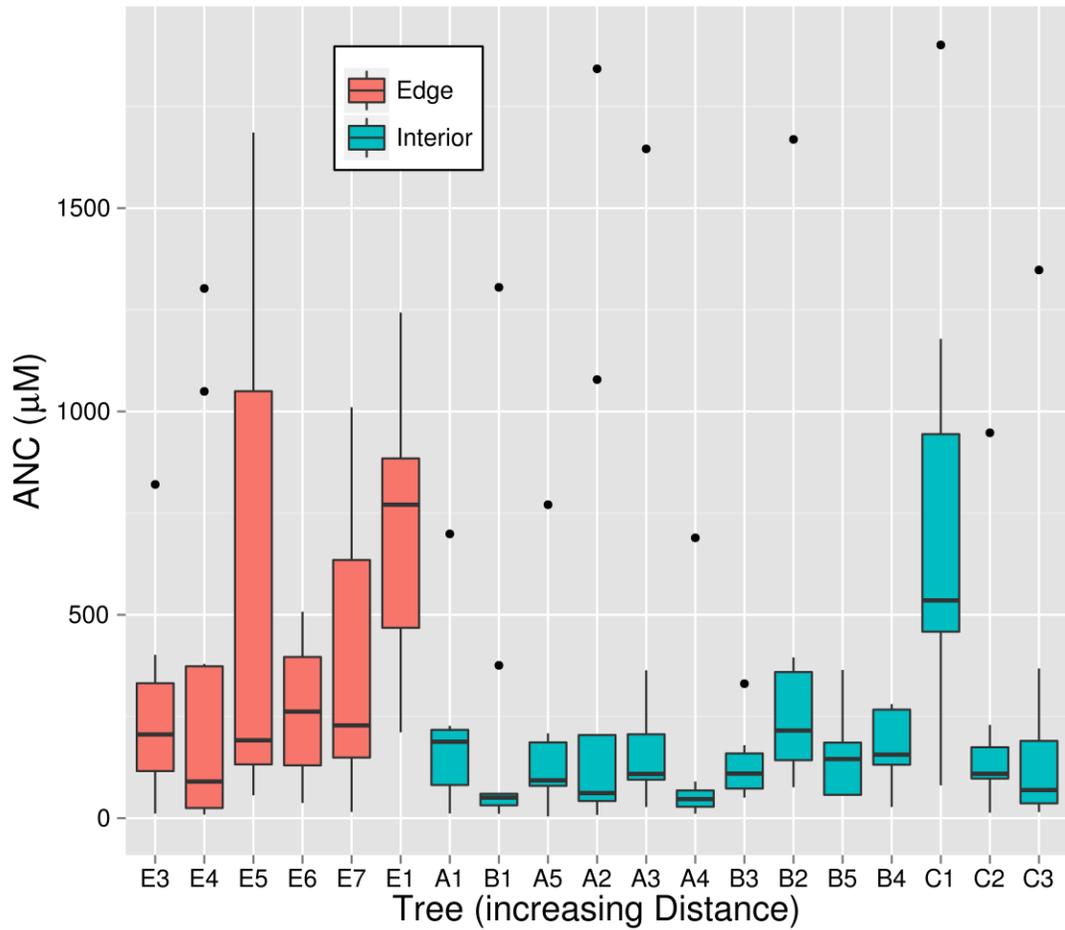
Figure 3. Comparison of stemflow acid neutralization capacity for all *L. tulipifera*
trees sampled. Distance from forest edge increases left to right on the x-
axis. Boxes are bounded by the lower and upper quartiles, with the
median represented by a solid black line. Box tails extend to lowest or
highest data value within 1.5 times the interquartile range of the lower
and upper quartile, respectively. All values outside this range are
represented as outliers with dots. $n = 8$ for trees E5, B3, and C3; $n = 9$ for
trees A1, A2, B2, B4, B5, and C1; and $n = 10$ for trees E1, E3, E4, E6,
E7, A3, A4, A5, B1, and C2.

3.2 pH

As with stemflow ANC, edge trees had a significantly greater ($p < 0.01$) stemflow pH than interior trees, with values of 6.86 and 6.47, respectively (Figure 4). These values are higher than those reported for *Pinus banksiana* Lamb. (jack pine) and *Populus tremuloides* Michx. (trembling aspen) by Jung and Chang (2013), for *Fagus sylvatica* L. (European beech) by Chang and Matzner (2000), and for China fir and hardwood stands by Wang et al. (2004), reinforcing the well-known correlation between tree species and stemflow acidity, and particularly the basifying effect of *L. tulipifera* (e.g., de Vries et al., 2007; Levia et al., 2011b). However, these values are also higher than the median stemflow pH value reported for *L. tulipifera* at the same site by Levia et al. (2011b), which is a testament to the overriding importance of individual event and tree characteristics in determining stemflow chemistry. The interquartile deviation of stemflow pH was also greater for edge trees than interior trees, with values of 0.72 and 0.64, respectively (Figure 4).

The trend in stemflow pH for individual trees is difficult to discern. The highest median stemflow pH of 7.46 was observed for tree "C1", located very far from the forest edge (Figure 5). Meanwhile, at a value of 6.27, tree "E4" had a lower median pH than all but three of the interior trees (Figure 5). The variability in stemflow pH was also more comparable between edge and interior trees than the stemflow ANC, with many interior trees having greater interquartile deviations than edge trees "E1", "E3", and "E6" (Figure 5). Interestingly, tree "C3" exhibited the highest variability in stemflow pH of the interior trees, whereas tree "C1" had the highest variability in stemflow ANC. In general, however, edge trees tended to have more basic stemflow than interior trees.

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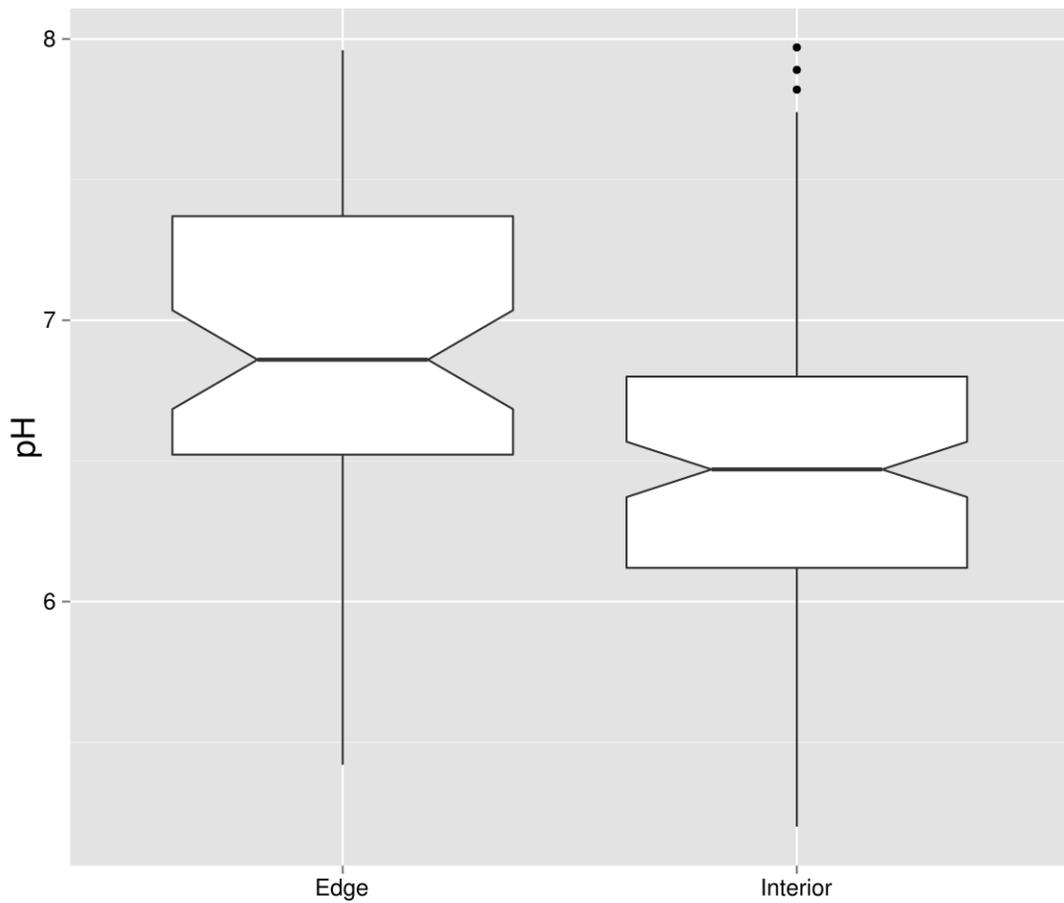
Figure 4. Comparison of stemflow pH of L. tulipifera trees located at the forest edge and in the forest interior. Boxes are bounded by the lower and upper quartiles, with the median represented by a solid black line. The ends of notches are calculated $X + 1.58 \text{ IQR} \div n^{1/2}$ (where X is the median, IQR is the interquartile range, and n is the sample size), with non-overlapping notches a likely indication of statistical significance (Chambers et al. 1983). Box tails extend to lowest or highest data value within 1.5 IQR of the lower and upper quartile, respectively. All values outside this range are represented as outliers with dots. $n = 58$ for edge trees and $n = 120$ for interior trees.
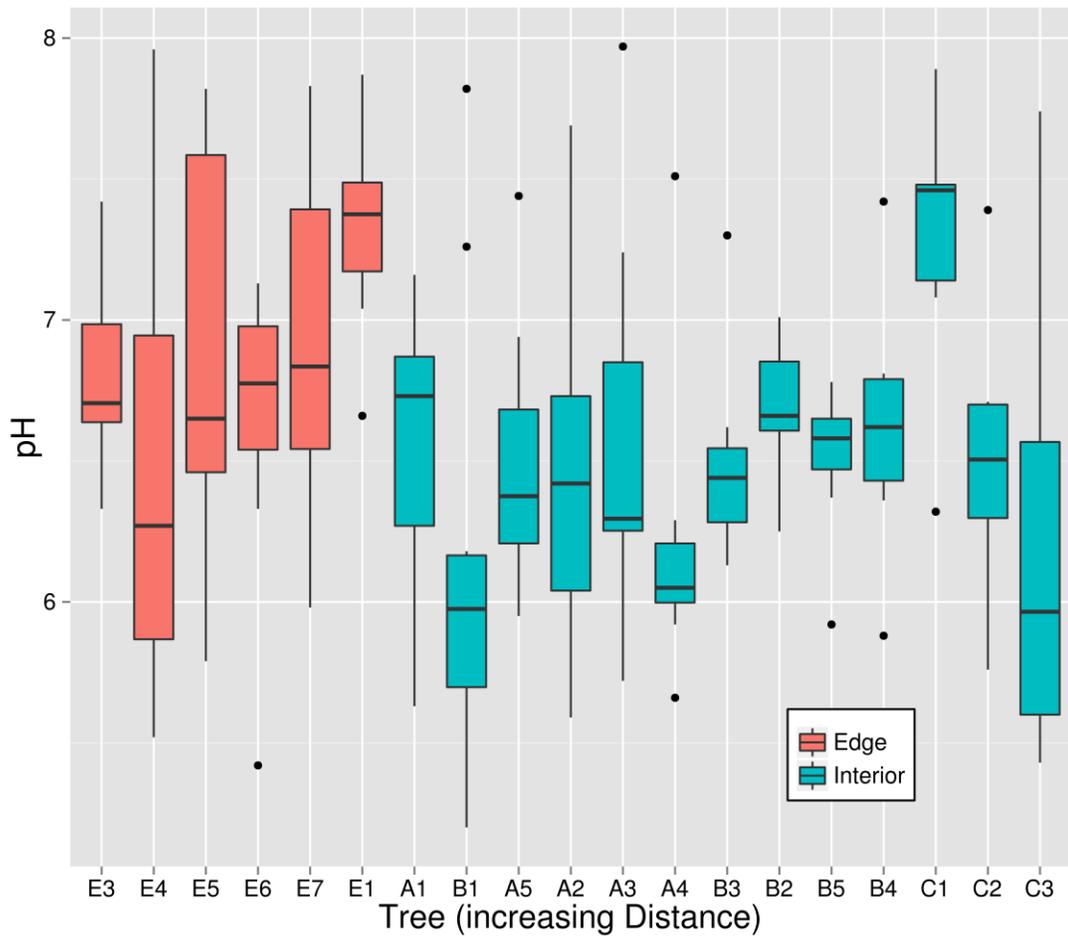
Figure 5. Comparison of stemflow pH for all *L. tulipifera* trees sampled. Distance from forest edge increases left to right on the x-axis. Boxes are bounded by the lower and upper quartiles, with the median represented by a solid black line. Box tails extend to lowest or highest data value within 1.5 times the interquartile range of the lower and upper quartile, respectively. All values outside this range are represented as outliers with dots. $n = 8$ for trees E5, B3, and C3; $n = 9$ for trees A1, A2, B2, B4, B5, and C1; and n = 10 for trees E1, E3, E4, E6, E7, A3, A4, A5, B1, and C2.

## 3.3   pH vs. ANC

Given the labor-intensive nature of determining ANC by titration, the possibility of modeling ANC as a function of pH was investigated. For an ideal

solution with only OH^- ions contributing to alkalinity, the following linear relationship should hold: $pOH = 14 - pH = -\log(ANC)$; i.e. $\log(ANC) = pH - 14$ (van Loon and Duffy, 2011). A plot of the natural logarithm of ANC as a function of pH for all samples is shown in Figure 6. The linear regression line has slope 0.82 and constant term -3.26 ($R^2 = 0.814$, $p < 0.01$). The larger (less negative) constant term and smaller coefficient on pH indicates significant deviation from ideal behavior, possibly caused by interactions between different solution components. For instance, Wang et al. (2004) observed stemflow sample titration curves for Chinese fir to have multiple inflection points and suggested the existence of phenolic OH and COOH groups on humic polymers dissolved in solution as an explanation.

For both edge and interior trees, the model was an underestimate of observed stemflow ANC for ~60% of observations and an overestimate for ~40% of observations. However, neither edge nor interior trees varied significantly from the line or from each other ($\chi^2 < 2.4$), suggesting an absence of systematic bias in the model. Furthermore, the simplicity of the model indicates that pH can be used as an effective proxy for acid neutralization capacity where methodological constraints prevent its direct measurement.
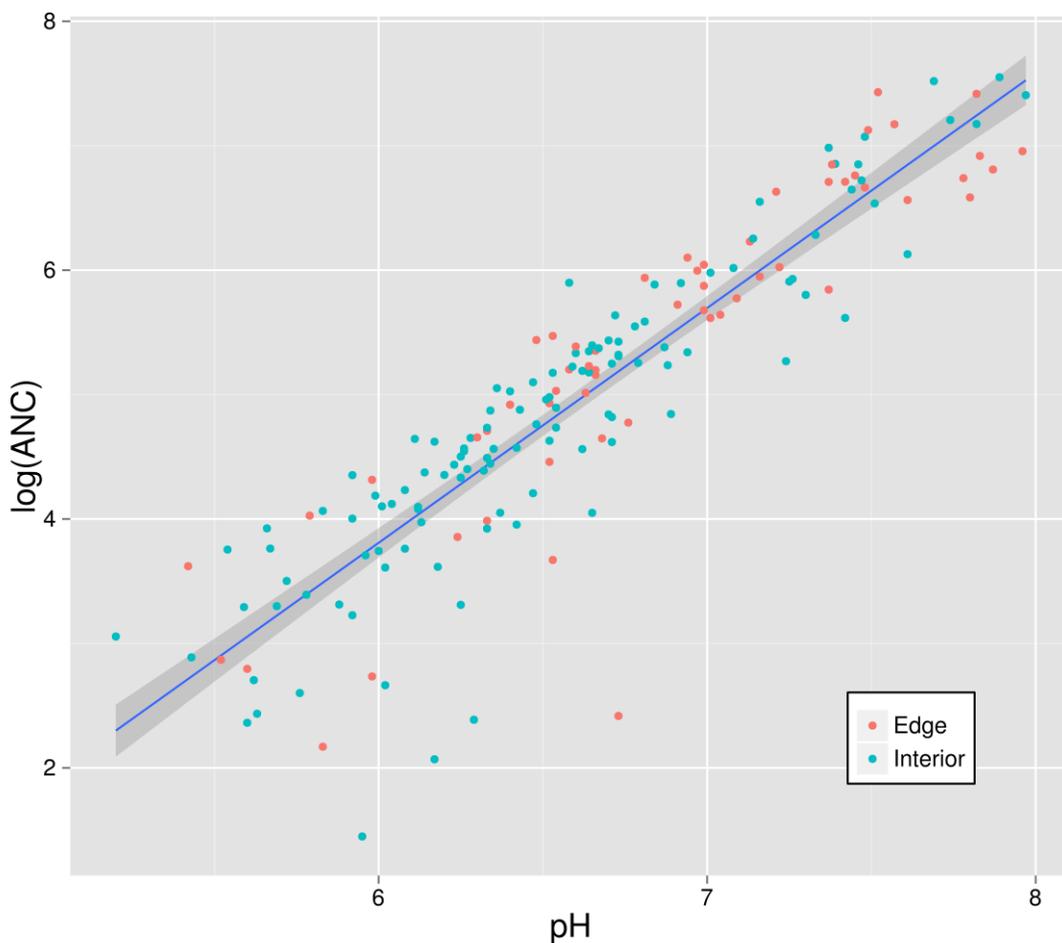
Figure 6. Base 10 logarithm of stemflow acid neutralization capacity as a function of pH with linear least-squares regression and 95% confidence interval (shaded). Regression equation is: log (ANC) = 0.82 (pH) − 3.26 (R^2 = 0.814, $p < 0.01$, $n = 178$).

3.4   Correlation analysis

Both stemflow pH and ANC were observed to be significantly and negatively correlated with stemflow volume (pH: $R^2 = -0.327$, $p < 0.01$; ANC: $R^2 = -0.296$, $p < 0.01$) and funneling ratio (pH: $R^2 = -0.272$, $p < 0.01$; ANC: $R^2 = -0.302$, $p < 0.01$). This can be explained by the observed exponential decay in washoff of dry deposition

reported by Levia et al. (2011b). Most accumulated dry deposition is washed off by new stemflow, and consequent flow is much less concentrated, causing dilution of bulk samples with increasing stemflow volumes. Stemflow volume was positively correlated with rainfall amount ($R^2 = 0.442$, $p < 0.01$) and duration ($R^2 = 0.235$, $p < 0.01$ but not with rainfall intensity), whereas ANC and pH were not correlated with duration but negatively correlated with intensity (ANC: $R^2 = -0.191$, $p < 0.01$; pH: $R^2 = -0.385$, $p < 0.01$). Stemflow ANC was positively correlated ($R^2 = 0.147$, $p < 0.01$), with relative humidity. Funneling ratio was observed to be weakly negatively correlated with the height-trunk circumference product ($R^2 = -0.361$, $p < 0.01$).

Neither stemflow ANC nor pH was correlated with the height-trunk circumference product used by André et al. (2008) (Figure 7). The absence of a correlation may be partly attributable to some methodological differences between André et al. (2008) and the present study: (1) André et al. (2008) specifically examined the height-trunk circumference product in relation to stemflow fluxes, dry deposition, and canopy exchange, which are related to but substantially different from ANC; and (2) André et al. (2008) estimated these dry deposition and canopy exchange via a regression approach, unlike the direct measurements via titration used in this study. It also is important to note that most of the significant correlations observed by André et al. (2008) were for smooth-barked *F. sylvatica*, with far fewer correlations for the rougher-barked *Quercus petraea* Liebl. (sessile oak) during the leafless period and almost no correlations for the latter during the leafed period. Finally, there is a fundamental difference in the setting of the two studies, with André et al. (2008) working in Belgium under higher levels of background deposition as compared to the relatively pristine environment at our study site. It, therefore, follows that we found no

significant correlation between stemflow ANC or pH and height-trunk circumference product for the similarly rough-barked *L. tulipifera*.

The differences between the results of André et al. (2008) and this study reinforce the notion that stemflow volume and chemistry are highly contextual, with many key processes dictated by climate, tree species, individual tree characteristics, and location (e.g., Neal et al., 1994; Levia and Frost, 2006; André et al., 2007; Chiwa et al., 2010; Levia et al., 2011a). For instance, it is likely that in forest stands located near atmospheric pollution sources, edge trees may actually have lower ANC and pH as a result of increased deposition of acid anions. In concert with Neal et al. (1994), we conclude that the differences in stemflow chemistry between edge and interior trees are representative of the surrounding environment. This is to say that whether the forest edge serves to diminish, neutralize, or enhance stemflow ANC and pH is a function of a suite of both biotic and abiotic factors, including human activity and canopy structure of the given locality.
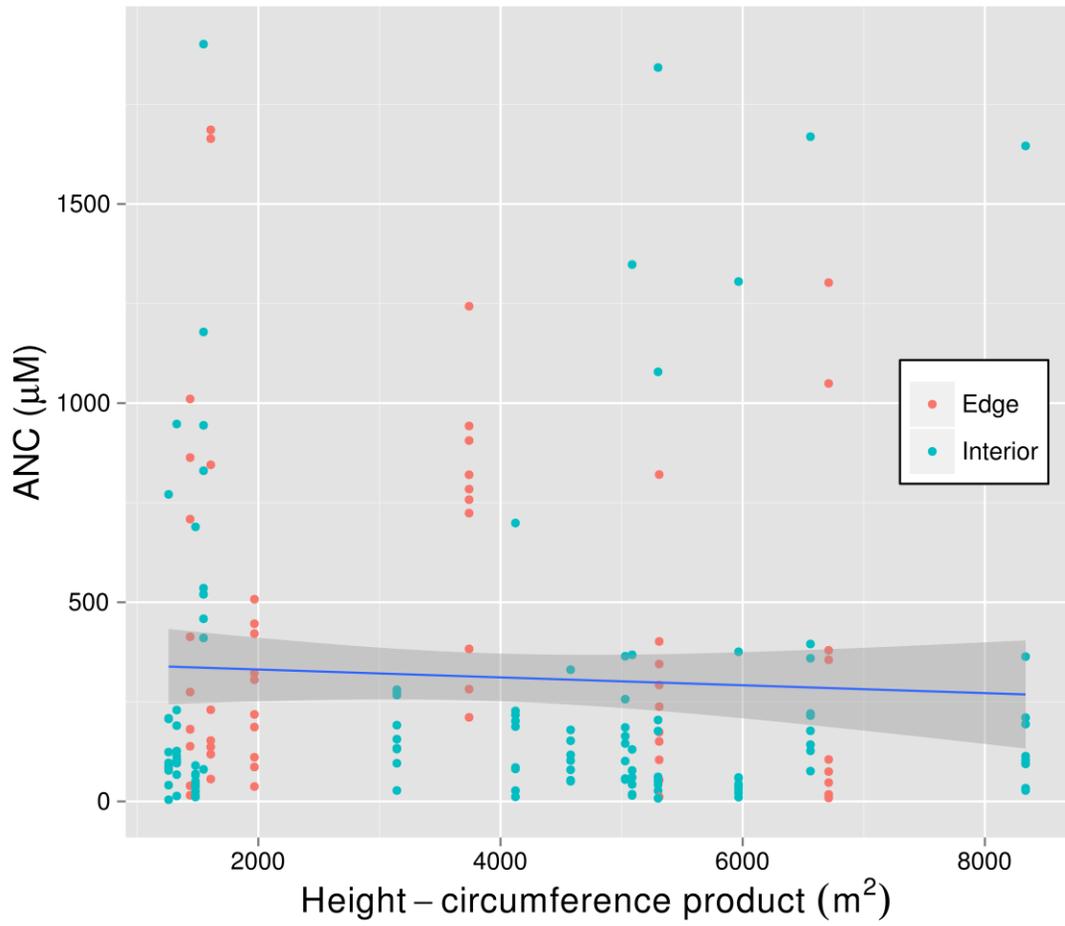
Figure 7. Stemflow acid neutralization capacity as a function of tree height-trunk circumference product with linear least-squares regression and 95% confidence interval (shaded) ($R^2 = -0.053$, $p = 0.480$, $n = 178$).

Chapter 4

CONCLUSION

This research demonstrates a quantifiable difference in stemflow ANC and pH between trees on the forest edge and interior. For *L. tulipifera* stands in an environment removed from industrial influences, stemflow is more basic and has a higher acid neutralization capacity at the edge than the interior, which we suggest is attributable to the dominance of cationic dust and ammonia in atmospheric deposition in these settings. The edge effect in stemflow ANC was greater than any reported for throughfall in previous studies (e.g., De Schrijver et al., 2007), which reaffirms the importance of stemflow to biogeochemical hot spots in forested ecosystems. Ultimately, the positive ANC values and high pH values for almost all stemflow samples in this study indicate that trees contribute to the ecosystem service of acid neutralization, which is critically important to long term ecosystem health. Further research on the ANC of other tree species common in both rural and urban areas with different edge characteristics is recommended to shed further light on biosphere-atmosphere interactions.

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